NAFTA-GAZ

Nafta-Gaz 2021, no. 5, pp. 293–298, DOI: 10.18668/NG.2021.05.02

Crystallization of simonkolleite ($Zn_5Cl_2(OH)_8 \cdot H_2O$) in powder samples prepared for mineral composition analysis by quantitative X-ray diffraction (QXRD)

Krystalizacja simonkolleitu ($Zn_5Cl_2(OH)_8 \cdot H_2O$) w preparatach proszkowych do analizy ilościowej składu mineralnego (QXRD)

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ABSTRACT: The analysis of mineralogical composition by quantitative X-ray diffraction (QXRD) is one of the standard research methods used in hydrocarbon exploration. In order to improve it and to obtain better results, the methodology of quantitative analysis used at Well Logging Department is being periodically (more or less) modified. After the introduction of the improvements, comparative analyses were performed on archival samples. Reflections from an unidentified phase which did not occur in the tested Rotliegend sandstone samples were noticed on X-ray diffractograms of archival samples. Reflections of a mineral called simonkolleite were identified in the X-ray diffraction database. Chemically it is a hydrated zinc chloride of the formula: $Zn_5Cl_2(OH)_8 \cdot H_2O$. Analysis of the composition of samples in which simonkolleite crystallised, indicated that the mineral is being formed in the result of the slow reaction of zinc oxide with halite (NaCl) and water vapour. An attempt was made to determine the influence of the presence of this mineral on the results of the quantitative analysis of mineralogical composition. The above methodology was applied on a group of ten samples. The results of the quantitative analysis conducted for archival samples stored with added zincite standard containing simonkolleite and for new, freshly grinded (without artifact) samples were compared. The comparison of the obtained results showed a slight influence of this mineral on the quantitative composition of the remaining components. The difference between the results usually did not exceed the method error. At the same time a significant difference in the calculated content of the internal standard was noted – on average 1% less in archival than in new samples. This shows that the reaction occurring in the archival samples will affect the evaluation of the quality of the obtained quantitative analysis, at the same time excluding the possibility of determining the rock's amorphous substance content with the internal standard method.

Key words: zincite, simonkolleite, quantitative X-ray diffraction, Rietveld method

STRESZCZENIE: Analiza ilościowa składu mineralogicznego (QXRD) jest jedną z podstawowych analiz mineralogicznych przeprowadzanych w celu rozpoznania skał przewiercanych w czasie poszukiwania złóż węglowodorów. Do metodyki analizy ilościowej stosowanej w Zakładzie Geofizyki Wiertniczej okresowo wprowadzane są (mniejsze lub większe) zmiany mające na celu jej udoskonalenie i uzyskiwanie lepszych rezultatów. Po tego rodzaju zmianach wykonywane są analizy porównawcze na próbkach archiwalnych. W trakcie przeprowadzania takiej serii analiz próbek archiwalnych – na dyfraktogramach rentgenowskich zauważono refleksy od niezidentyfikowanej fazy, która nie występowała w badanych próbkach czerwonego spągowca. Po przeszukaniu bazy danych dyfrakcji rentgenowskiej zidentyfikowano refleksy minerału o nazwie simonkolleit. Chemicznie jest to uwodniony chlorek cynku o wzorze $Zn_5Cl_2(OH)_8 \cdot H_2O$. Po przeanalizowaniu składu próbek, w których doszło do krystalizacji simonkolleitu, stwierdzono, że powstaje on wskutek powolnej reakcji tlenku cynku z halitem (NaCl) przy obecności pary wodnej. Na grupie 10 próbek wykonano próbę określenia wpływu obecności tego minerału na wyniki analizy ilościowej składu mineralogicznego według stosowanej metodyki. Porównano wyniki analizy ilościowej dla preparatów archiwalnych przechowywanych z dodanym wzorcem, w których występował simonkolleit, oraz dla preparatów nowych po powtórnym zmieleniu nowej porcji próbki (bez artefaktu). Zestawienie uzyskanych wyników pokazało niewielki wpływ obecności tego minerału na ilościowy skład pozostałych składników badanych próbek. Błąd pomiędzy analizami zazwyczaj mieścił się w granicach błędu metody. Jednocześnie zauważono istotną różnicę w obliczonej zawartości wzorca wewnętrznego – średnio o 1% mniej. To pokazuje, że zachodząca reakcja w próbkach archiwalnych będzie wpływała na ocenę jakości uzyskanych wyników analizy ilościowej i jednocześnie wyklucza możliwość określenia metodą wzorca wewnętrznego zawartości substancji amorficznej w skale.

Słowa kluczowe: cynkit, simonkolleit, ilościowa analiza składu mineralogicznego, metoda Rietvelda

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Article contributed to the Editor: 22.11.2020. Approved for publication: 23.04.2021

Introduction

The mineralogical composition analysis by quantitative X-ray diffraction (QXRD) based on Rietveld method (Rietveld, 1969) began to develop dynamically after about ten years from the publication of Rietveld's first work of 1967 (Rietveld, 1967; Tylor and Hinczak, 2006). The widespread use of QXRD to determine rocks mineral content occurred later, also in industry, with the emergence of computer software that has greatly facilitated the analysis.

There are many factors determining a good quantitative analysis: proper preparation of samples, correct calibration of the diffractometer and finally, in regard to the software, the best possible approximation of the measured and modelled diffractograms. The procedure of the quantitative analysis of mineralogical composition applied at the Well Logging Department includes a number of best practices used in mineralogical laboratories (Środoń et al., 2001; Omotoso et al., 2006). The applied procedure of sample preparation allows for their proper representativeness and minimization of the effect of crystallites preferred orientation. The correctness of the diffractometer calibration is being constantly checked by measurements of the reference material. The Siroquant program of recognized usefulness in regard to the rock samples analysis, including those containing clay minerals (Kowalska, 2013), is applied to calculate the model diffractograms. The QXRD is employed in the Well Logging Department to control and calibrate results from other analytical methods and in order to develop mineralogical – petrophysical models (Zagórska et al., 2016; Skupio et al., 2020).

An internal standard is added to a sample as a rule in the applied methodology of quantitative analysis. Two minerals, zincite (ZnO) and corundum (Al_2O_3) are commonly used as internal standards in research laboratories. Adding a certain amount of the internal standard to a sample serves not only as a quality control of the results but can also allow to determine the amorphous substance content of the tested sample.

Problem description

The quantitative X-ray analysis of mineral composition is one of the routine analyses at the Well Logging Department of the Oil and Gas Institute – National Research Institute. It is performed in two stages. The first one is to recognize the sets of diagnostic reflections of minerals forming the examined rock, i.e. the qualitative analysis. The second stage is to perform the quantitative analysis with the use of software and to verify whether all the reflections have been covered and a satisfactory conformity between the measured and modelled diffractograms has been achieved.

Along with the introduction of QXRD methodology improvements, a large group of archival samples of Rotliegend sandstone was analysed at the Well Logging Department. The research was planned in order to compare the obtained results and to analyse the differences between two quantitative analysis programs (RockJock and Siroquant). Some of the analysed samples were previously mixed with the internal standard. After the measurements the samples are most often stored according to accreditation requirements, hence the possibility of re-analysing of the archival samples. Samples for the QXRD analysis were prepared using the side-loading method, and measured in the range of 5–65° 2Θ. Reflections from an unknown phase, not present on the previously measured X-ray diffractograms, were observed on some of the X-ray diffractograms obtained in this way. The diffractogram of one of these samples together with a series of reflections not identified during the preliminary qualitative analysis is shown on Figure 1.

As the work progressed, it turned out that when it regards the problem of the unidentified phase a larger group of samples is concerned (examples shown on Fig. 2). Therefore the Powder Diffraction File (PDF) database of the International Centre for Diffraction Data Centre (ICDD) was searched in order to identify the unknown mineral. As the mineral composition of the samples was previously known and the analyses were of comparative nature, it was clear that this unidentified phase or mineral must have been some kind of an artefact or was formed secondarily in the XRD specimen as the result of the sample's components reaction.

After searching the database the diagnostic reflections were identified. The mineral was recognised as simonkolleite, hydrated zinc chloride of chemical formula $Zn_5Cl_2(OH)_8 \cdot H_2O$ (Tab. 1). X-ray diffractogram of sample A1 with described reflections positions is shown on Figure 3.

In order to explain the crystallization of simonkolleite in the selected set of samples, the chemical and mineral composition of the tested samples was analysed taking into account that this mineral was crystallized only in a part of the analysed samples. The Rotliegend sandstone samples are characterized by high salinity of reservoir fluids and frequent presence of halite (NaCl). Halite, due to its physical properties, often undergoes partial or complete amorphization and dissolution during the sample preparation for QXRD analyses. One of the diagnostic reflections of halite (Hl) is visible, in an archival sample (Fig. 3), what confirms the presence of halite. The strongest halite reflection (100) interferes with a zincite reflection.

Taking into account the presence of sodium chloride – halite and the used internal standard i.e. zinc oxide (zincite), it was concluded that with time a reaction occures in the samples, in which hydrated zinc chloride – simonkolleite crystallizes

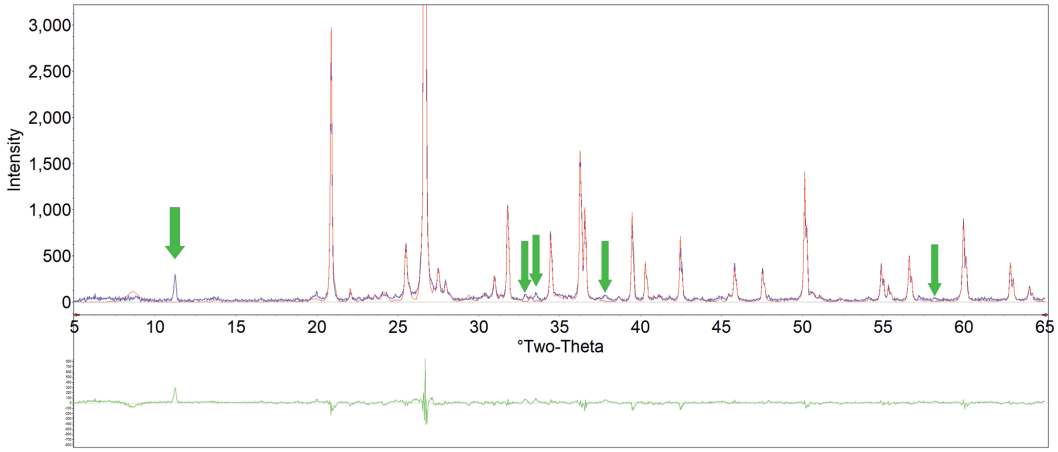

Fig. 1. Diffractogram of sample A1 with reflections from an unknown crystalline phase (green arrows) – no standard present in the SiroQuant program; blue colour – original diffractogram of the archvial sample; red colour – model diffractogram; green colour below – differential diffractogram

Rys. 1. Dyfraktogram próbki A1 z zaznaczonymi refleksami od nieznanej fazy krystalicznej (zielone strzałki) – brak wzorca w programie SiroQuant; kolor niebieski – dyfraktogram oryginalny próbki; kolor czerwony – dyfraktogram modelowy; kolor zielony poniżej – dyfraktogram różnicowy

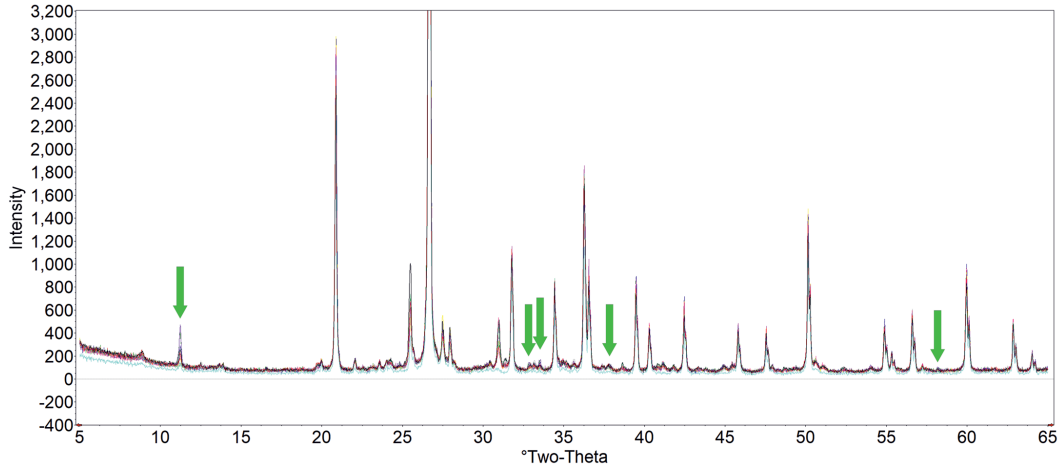

Fig. 2. Diffractograms of eleven sandstone samples with marked reflections (green arrows) from an unknown phase

Rys. 2. Dyfraktogramy 11 próbek piaskowców z zaznaczonymi refleksami (zielone strzałki) od nieznanej fazy

from NaCl and ZnO substrates, most probably according to the general equation given by Sithole et al. (2012):

$$5Zn^{2+} + 8OH^{-} + 2Cl^{-} + H_2O \rightarrow Zn_5(OH)_8Cl_2 \cdot H_2O$$

According to the current knowledge of the authors, this problem has not yet been described in scientific journals. Most of the literature in which simonkolleite is mentioned is rather concerned with the synthesis of zinc oxide from this mineral as a substrate (e.g., Zhang and Yanagisawa, 2007; Moezzi et al., 2016).

Simonkolleite is found as a product of weathering of slag and other zinc-containing ore waste and also as a product of metals corrosion and zinc containing metal objects. It is also used as food supplementfor farm animals. This mineral crystallises in the hexagonal system and has an excellent cleavage on {001} plane.

Table 1. Simonkolleite diagnostic reflections (International Centre for Diffraction Data (ICDD) Powder Diffraction File no. 7-155; de Wolff, P., Technisch Physische Dienst, Delft, The Netherlands)

Tabela 1. Refleksy diagnostyczne simonkolleitu (International Centre for Diffraction Data (ICDD) Numer karty w bazie PDF: 7-155; de Wolff, P., Technisch Physische Dienst, Delft, Holandia)

Distance between planes – d	Intensity
7.87 Å	(100)
3.58 Å	(30)
3.17 Å	(40)
2.94 Å	(30)
2.73 Å	(60)
2.67 Å	(70)
2.37 Å	(40)
1.59 Å	(40)

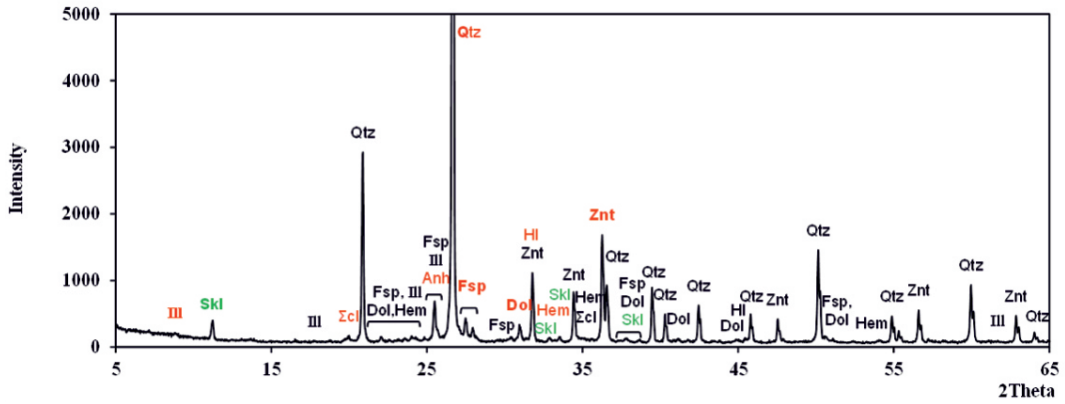

Fig. 3. X-ray diffractogram of the A1 sandstone sample in which the simonkolleite crystallised. Abbreviations: Qtz – quartz, Fsp – feldspar group, Dol – dolomite, Anh – anhydrite, Hem – hematite, Hl – halite, Ill – illite, Σcl – sum of clay minerals, Znt – zincite (internal standard), Skl – simonkolleite

Rys. 3. Dyfraktogram rentgenowski próbki A1 piaskowca, w którym wykrystalizował simonkolleit. Objaśnienia skrótów: Qtz – kwarc, Fsp – grupa skaleni, Dol – dolomit, Anh – anhydryt, Hem – hematyt, Hl – halit, Ill – illit, Σcl – suma minerałów ilastych, Znt – cynkit (wzorzec wewnętrzny), Skl – simonkolleit

Effect of the presence of simonkolleite on the results of quantitative analysis

In order to assess the influence of the observed phenomenon of simonkolleite crystallization in archive samples on the results of quantitative analysis of rocks, QXRD analyses were performed for ten samples. The previously mentioned Rotliegend sandstones in which diagnostic reflections of this mineral were easily observed were used. The analysis was performed according to the PBN-06/SW-1 test procedure.

A set of archival samples mixed with zincite and samples grounded with zincite immediately before the XRD measurement (marked as a new sample in Table 2) were analysed. The results are presented in Table 2.

In the analysed samples the influence of the crystallized mineral (simonkolleite) on the calculated mineral contents can be considered quite small. The relative error of the XRD method is usually accepted as 5–10% depending on the complexity of the mineral composition of the sample. Therefore, one should be aware that 0.5% of the absolute value for minerals occur-

Table 2. Results of quantitative analysis of 10 samples

Tabela 2. Wyniki analizy ilościowej dla 10 próbek

Sample		Qtz	Dol	Anh	Hem	Hl	Ab	Kfs	Ill	Ms	Chl
1	New	71.3	3.4	3.2	1.5	0.7	5.9	7.7	4.7		1.6
	Archival	71.4	3.2	3.1	1.6	0.6	5.9	7.5	4.9		1.7
	Difference	–0.1	0.2	0.1	–0.1	0.1	0	0.2	–0.2		–0.1
	St deviation	0.07	0.14	0.07	0.07	0.07	0.00	0.14	0.14		0.07
2	New	72.8	3.6	2.5	1.5	0.7	6	7.3	5.5		
	Archival	73.5	3.4	2.6	1.5	0.5	5.3	7.4	5.8		
	Difference	–0.7	0.2	–0.1	0	0.2	0.7	–0.1	–0.3		
	St deviation	0.49	0.14	0.07	0.00	0.14	0.49	0.07	0.21		
3	New	69.9	5.4	3.6	1.4	0.7	6.2	7.2	4.2		1.3
	Archival	69.2	5.1	3.8	1.7	0.7	6.2	6.3	5.4		1.6
	Difference	0.7	0.3	–0.2	–0.3	0	0	0.9	–1.2		–0.3
	St deviation	0.49	0.21	0.14	0.21	0.00	0.00	0.64	0.85		0.21
4	New	70	2.5	9.5	0.9	0.5	5.8	6.2	4.7		
	Archival	71.2	2.3	9.5	0.8	0.7	5.4	4.8	5.3		
	Difference	–1.2	0.2	0	0.1	–0.2	0.4	1.4	–0.6		
	St deviation	0.85	0.14	0.00	0.07	0.14	0.28	0.99	0.42		

cd. Tabela 2/ cont. Table 2

Sample		Qtz	Dol	Anh	Hem	Hl	Ab	Kfs	Ill	Ms	Chl
5	New	70.4	3.3	1.9	1.9	0.6	6.3	7.2	4.1	4.4	
	Archival	71.4	2.8	1.8	1.3	0.6	6.4	7.8	4.7	3.1	
	Difference	–1	0.5	0.1	0.6	0	–0.1	–0.6	–0.6	1.3	
	St deviation	0.71	0.35	0.07	0.42	0.00	0.07	0.42	0.42	0.92	
6	New	65.1	2.2	1.5	3.3	0.6	4.7	7.1	7.1	5.2	3.1
	Archival	67.6	2.6	1.4	2.9	0.6	4.5	7.1	6.8	4	2.4
	Difference	–2.5	–0.4	0.1	0.4	0	0.2	0	0.3	1.2	0.7
	St deviation	1.77	0.28	0.07	0.28	0.00	0.14	0.00	0.21	0.85	0.49
7	New	72.2	0.6	1.8	1.5	1.2	6.1	9.2	7.5		
	Archival	75.7	0.6	1.8	1.6	0.8	6.2	8.4	4.9		
	Difference	–3.5	0	0	–0.1	0.4	–0.1	0.8	2.6		
	St deviation	2.47	0.00	0.00	0.07	0.28	0.07	0.57	1.84		
8	New	71.7	2.1	2.3	1.9	0.7	6	8	5.7		1.6
	Archival	72.5	2.1	2.4	2	0.5	6	7.2	5.5		1.7
	Difference	–0.8	0	–0.1	–0.1	0.2	0	0.8	0.2		–0.1
	St deviation	0.57	0.00	0.07	0.07	0.14	0.00	0.57	0.14		0.07
9	New	63.7	4	3.2	2.8	0.7	4.7	6.9	7.6	4.3	2.2
	Archival	64.5	3.7	3.2	3	0.5	4.9	6.3	7.1	4.5	2.2
	Difference	–0.8	0.3	0	–0.2	0.2	–0.2	0.6	0.5	-0.2	0
	St deviation	0.57	0.21	0.00	0.14	0.14	0.14	0.42	0.35	0.14	0.00
10	New	65.4	4.9	4.6	1.9	0.7	5.9	7	3.6	4.7	1.4
	Archival	65.9	4.5	4.5	2	0.4	5.4	6.5	5	4	1.7
	Difference	–0.5	0.4	0.1	–0.1	0.3	0.5	0.5	–1.4	0.7	–0.3
	St deviation	0.35	0.28	0.07	0.07	0.21	0.35	0.35	0.99	0.49	0.21

Abbreviations: Qtz – quartz, Dol – dolomite, Anh – anhydrite, Hem - hematite, Hl – halite, Ab – albite, Kfs – potassium feldspar, Ill - illite, Ms – muscovite, Chl – chlorite

ring in the amount <10% and 2% of the absolute value for minerals occurring in the amount >30% can be considered an error. Taking that into consideration, it can be concluded that a significantly different result was obtained only in 10 cases out of 90 (Tab. 2). In order to present the differences in the obtained results, the table also includes the standard deviation values (in 14 cases out of 90 exceeds 0.5).

The calculated content of the internal standard (ZnO) in the archival samples and in those grounded directly before the measurement (new samples) was also analysed. According to the adopted quantitative analysis methodology 10% zinc chloride is added to the samples. Table 3 contains the results of ZnO content calculated for both sets of samples. It can be seen that in new samples the content of ZnO is close to 10% within acceptable limits, while in archival samples it is on average more than 1% lower. Only for samples from number 8 to 10 in which the simonkolleite reflections were very small the

Table 3. Calculated contents of ZnO (zincite) in archival and new sample

Tabela 3. Obliczony udział ZnO (cynkitu) w próbkach archiwalnych i nowych

Sample	% ZnO in new sample	% ZnO in archival sample	Difference
1	9.728	7.700	2.028
2	9.635	8.485	1.150
3	9.580	8.425	1.155
4	9.335	8.220	1.115
5	9.355	8.394	0.961
6	10.034	7.960	2.074
7	9.360	7.635	1.725
8	9.510	8.840	0.670
9	9.390	8.860	0.530
10	9.452	9.085	0.367

difference is less than 1%, but still quite significantly deviates from 10%. As mentioned earlier, the zinc content is monitored for the purpose of the results quality control, and in regard to samples in which an amorphous substance is present it allows to calculate its percentage. In the case of archival samples, the calculated amount of ZnO neither meets the quality control criterion nor makes it possible to estimate the content of amorphous substance.

Summary and conclusions

Crystallization of simonkolleite in archival samples mixed with zincite was confirmed on the basis of a set of diagnostic reflections of the mineral. This mineral was formed as a result of the reaction of zinc oxide with sodium chloride and water vapour. As the comparative analyses have shown, this reaction has a significant impact on the zincite content calculated by quantitative analysis (QXRD). A decrease in the amount of zincite may affect the quality assessment of the quantitative analysis and at the same time make the estimation of the amorphous substance impossible. However, comparison of the calculated remaining minerals contents showed that the influence of this process, on the tested set of samples, was small and in most cases did not exceed the accepted limits of the method error.

The observed process leads to the conclusion that in order to maintain the highest standards of analysis, the X-ray diffraction measurements should be performed shortly after mixing the sample with an internal standard (ZnO), especially if the sample contains chlorides that could react with zincite. At the same time it seems unreasonable to store samples mixed with ZnO if its decomposition or reaction with the sample is possible. For chloride-rich samples, the use of corundum as an internal standard may be considered in order to avoid simonkolleite crystallisation.

This paper was written on the statutory work entitled: *Analiza proweniencji skał późnopaleozoicznych na podstawie datowania cyrkonu detrytycznego metodą U-Pb dla wybranego basenu sedymentacyjnego* – the work of the Oil and Gas Institute – National Research Institute was commissioned by the Ministry of Science and Higher Education; order number: 0031/SW/2020, archive number: DK-4100-0019/2020.

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